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ELEMENTARY NITROGEN

JOHNSON

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ON CERTAIN INDICATIONS OF THE EXISTENCE OF AN ALLOTROPIC MODIFICATION OF

ELEMENTARY NITROGEN

AND ON THE

SYNTHESIS OF AMMONIA

BY

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LONDON
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11 NEW BURLINGTON STREET
1885

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PREFACE.

EARLY in the year 1881, I read two papers before the Chemical Society on the "Synthesis of Ammonia," which are published in the "Chemical Society's Journal" for March, 1881.

Since that date I have read two papers on the same subject before the Chemical Society, and one before the Royal Society, which have not been published.

The reason of this is not far to seek. My researches have not produced results which are of sufficiently convincing nature to force the acceptance of my conclusions upon the scientific mind, and, in the absence of such compulsion, they are little likely to receive universal acknowledgment, opposed as they are to preconceived ideas and theories. Indeed, at this distance of time, and surveying the past with calm consideration, I am able to appreciate the caution of those learned societies, which have refused to give the sanction of their names to work that might ultimately prove to be erroneous, and for the errors of which they would, perhaps, consider themselves responsible.

But, however commendable this extreme caution may be in the case of a society, the conduct of an individual should, to my mind, be governed by different laws.

The solitary observer knows—what others cannot be aware of—the exactness and perseverance with which his questions have been laid before nature, and their answers recorded. He has the faith in himself and his work which others cannot have; and he must not run the risk of allowing an important scientific fact to be lost, for fear of some possible slur upon his scientific reputation in case his conclusions prove to be erroneous.

Actuated by these motives, and believing as I do that the time will come when scientific men will repeat my experiments—not with a view to prove that I am in the wrong, but with the object of discovering the truth,—I have carefully prepared an exact statement of my work upon this subject, and of the conclusions to which it has led me at the present time; and I have been the more anxious to perform this task, since I have observed that, in consequence of the non-publication of my more recent papers, some very confused notions are prevalent among chemists as to what has been done hitherto.

As I am particularly anxious that this little book may not be regarded as in any way controversial, I have entirely omitted the names of those who have differed from me, feeling sure that those who have honoured me with their criticisms have already obtained sufficient publicity elsewhere. At the same time I have endeavoured to attribute to their authors all those historical facts connected with my subject which have been at my disposal.

February, 1885.

ON CERTAIN INDICATIONS OF THE EXISTENCE OF AN ALLOTROPIC MODIFICATION OF ELEMENTARY NITROGEN, AND ON THE SYNTHESIS OF AMMONIA.

CHAPTER I.

HISTORICAL ELECTRO-CHEMICAL RESEARCHES.

Historical Notice of Electro-Chemical Researches by—I. (a) Donkin; (b) Berthelot; II. Dehérain and Maquenne; P. and A. Thénard; III. H. Ste. Claire Deville.

I. Direct Synthesis of Ammonia by means of the Silent Discharge.

(a) *Mr. Donkin's Researches.*

In the "Proceedings of the Royal Society," XXI., 1873, pp. 281, 282, Mr. W. P. Donkin has described a method for demonstrating the formation of ammonia by direct synthesis under the influence of the silent discharge of electricity of high tension. The details of his experiment are as follows:—

Atmospheric nitrogen was very carefully separated from every trace of oxygen, passed into a glass gas-holder by displacement of water, and mixed there with three times its volume of pure hydrogen. The mixture was allowed to stand over the water for many hours (and to this fact I wish to draw particular attention), and was then passed through an induction-tube, made entirely of glass, and shaped as indicated in this diagram.

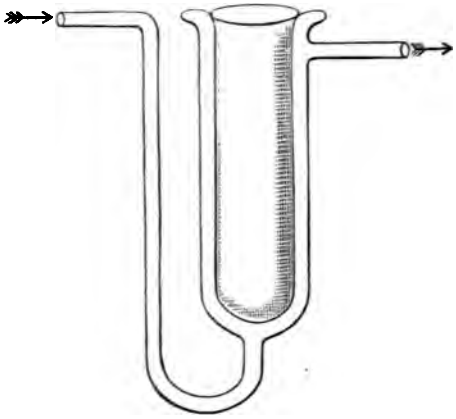

Fig. 1.

Mr. Donkin's nitrogen was freed from oxygen, first by phosphorus, then by red-hot metallic copper.

After standing over the water for many hours, the mixed nitrogen and hydrogen gases were transmitted through sulphuric acid, and then through the induction-tube, where they were acted upon by the silent discharge from a Ruhmkorff's coil. The issuing gas was found to contain small quantities of ammonia.

The result of this experiment indicates that combination of nitrogen and hydrogen gases may be brought about in sufficient quantities to enable the operator to demonstrate the formation of ammonia, even under the influence of the brief exposure to the silent electrical discharge to which the gases are subjected while *passing through* an induction-tube.

This experiment of Mr. Donkin's has not proved successful in the hands of all chemists who have repeated it, and I shall endeavour to account for these failures shortly. At present I will only remark that, in my opinion, they have been due to the omission of the precaution upon which I have laid so much stress—viz., the storage of the gases for many hours over water before subjecting them to the influence of the silent discharge.

(b) *Experiments of M. Berthelot.*

M. Berthelot's experiments (which are recorded in the "Comptes-Rendus," LXXXII., 1283, 1360) differ from those of Mr. Donkin in that he submitted a mixture of nitrogen and hydrogen gases to the prolonged action of the silent discharge, instead of merely causing the mixed gases to pass through a tube where they were transitorily subjected to its influence. M. Berthelot proved that, in the absence of an absorbent for ammonia, as much as 3 *per cent.* of the gaseous mixture could be made to combine, but no more.

II. OBSERVATIONS OF MM. DEHÉRAIN AND MAQUENNE, AND OF MM. P. AND A. THÉNARD, ON THE ACTION OF THE SILENT DISCHARGE UPON WATER-VAPOUR, AND UPON A MIXTURE OF NITROGEN GAS AND WATER-VAPOUR.

In the "Comptes-Rendus" (XCIII., 895), it has been shown by MM. Dehérain and Maquenne that water-vapour is, under certain circumstances, dissociated by the silent discharge, and this is particularly liable to occur when the induction-tube contains rarefied gas.

In the "Comptes-Rendus" (LXXXVI., 517, 1508), MM. P. and A. Thénard record that nitrogen gas, when subjected to the influence of the silent discharge in presence of aqueous vapour, disappears, and forms *ammonium nitrite*. This observation has been confirmed by Berthelot ("Bull. Soc. Chim." [2] xxvii. 338).

III. ACTION OF THE ELECTRIC SPARK.

Researches of M. H. Ste. Claire Deville.

The only experiment which I can find anywhere recorded, tending to throw doubt upon the universally accepted statement that "ammonia gas is totally and completely dissociated by a continued series of electric sparks," is one by H. Ste. Claire Deville (*vide* "Comptes-Rendus," 1865, LX., pp. 324 and 325). He found that when ammonia gas was confined over mercury and submitted to the action of a series of electric sparks, no matter how prolonged, dissociation was *never perfect*, *i.e.*, a trace of ammonia could always be detected in the residual gas by admitting into it a few bubbles of dry hydrochloric acid gas, when fumes of sal-ammoniac were invariably produced. He also found that a mixture of two volumes of hydrochloric acid gas, three volumes of hydrogen, and one volume of nitrogen was completely converted into sal-ammoniac by the transmission through the gaseous mixture of a series of electric sparks.

The above are the only researches having any bearing upon the subject of this memoir which I have been able to discover in scientific literature.

CHAPTER II.

RESEARCHES ON THE SYNTHESIS OF AMMONIA FROM THE GAS EVOLVED BY THE ACTION OF HEAT UPON SOLUTIONS OF AMMONIUM NITRITE.

Criticisms of Experiments detailed in "Chemical Society's Journal," March, 1881—Acid Ferrous Sulphate as an Absorbent for Nitric Oxide—Hydrogen passed through Solution of Silver Nitrate may become contaminated with Oxides of Nitrogen—Cupric Oxide not dissociated at Temperatures compatible with the integrity of Combustion Tubing—Purity of Nitrogen effected not by Ferrous Sulphate, but by Ferrous Hydrate—Experiments upon the Action of Ferrous Hydrate upon Nitric Oxide Gas—Hydrogen purified by Chromic Acid, &c., *vice* Silver Nitrate—Hydrogen mixed with *Heated* Nitrogen from Ammonium Nitrite gives no Ammonia—Gas from Ammonium Nitrite probably contains an Allotropic Modification of Nitrogen analogous to Ozone—Proofs of the Non-identity of the Ammonia-forming Gas (Active Nitrogen) from Ammonium Nitrite with any known Oxide of Nitrogen.

In my first experiments on the synthesis of ammonia I described an apparatus, figured in the March number of the "Chemical Society's Journal" for 1881, by means of which purified nitrogen, obtained from a boiling solution of ammonium nitrite, was mixed with hydrogen and passed through heated spongy platinum, with the result of the production of a small quantity of ammonia.

Two criticisms have been offered upon this experiment. First, it has been said that the reagent I employed to purify the nitrogen was incapable of absorbing nitric oxide completely; and, secondly, it has been averred that when hydrogen passes through a solution of silver nitrate, oxides of nitrogen are produced, and yield ammonia when the resulting gas is passed through tubes containing red-hot spongy platinum.

Now, as regards the question of the purity of the nitrogen obtained by means of the apparatus I employed—viz., a series of tubes containing pumice saturated with an acidulated solution of ferrous sulphate,—I consider that that is proved by the test employed by me for the purity of the gas—viz., the maintenance of a constant weight by a tube containing metallic copper heated to redness for one hour in a current of the purified nitrogen. The tube was an ordinary hard glass combustion tube, and I therefore do not consider an objection which has been raised to this test—viz., that copper oxide might have been formed and afterwards *dissociated*—as worthy of a moment's consideration. It is inconceivable that copper oxide could have been dissociated completely at a temperature low enough to be compatible with the integrity of the tube.

I consider, therefore, that the *purity of the nitrogen* was demonstrated in my published research; but there is great validity in the objection raised against the statement that the nitrogen was purified by means of a solution of *acid ferrous sulphate*. It is quite true that it is impossible to remove every trace of nitric oxide from nitrogen gas by means of that reagent when a current of the gas is kept passing through it. I fully explained the production of pure nitrogen by means of the apparatus figured by me, in an answer to the above criticism; but my explanation was not published, and, therefore, this part of the matter still remains in an unsatisfactory state.

The explanation is as follows:—

The first purifying apparatus through which the nitrogen from the heated ammonium nitrite solution was passed was a long horizontal tube (marked I in the diagram), which was packed with fragments of pumice-stone saturated with an acidulated solution of ferrous sulphate. Now, the originally colourless pumice-stone became gradually black at the extremity next to the flask, from which the nitrogen was escaping. This dark colour spread continuously along the tube, whilst the portion next to the flask again changed colour, becoming reddish-brown.

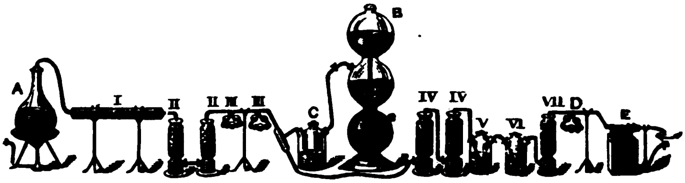

FIG. 2.*

It was not until these changes had advanced about one-third of the distance along the tube that the nitrogen gas escaping at the end of the apparatus was found to be free from all traces of oxide of nitrogen.

The explanation of these phenomena is simple. 1st. The dark blue or black colour observed in the pumice was due to the formation of *ferrous hydrate*, for the portion of the tube next to the generating flask was found to be strongly *ammoniacal.* The nitrogen from the hot ammonium nitrite solution contained ammonia, which first neutralized the acid present in the ferrous sulphate solution, and afterwards precipitated ferrous hydrate, which remained in the pores of the pumice. 2nd. The conversion of the ferrous hydrate into *ferric hydrate* (to which the formation of the reddish-brown colour was due), accompanied by the diminution and final cessation of the contamination of the nitrogen gas with oxides of nitrogen, indicates that probably the oxide of nitrogen originally present in the gas from the generating flask underwent *reduction* under the influence of the ferrous hydrate in the pumice, which it reciprocally *oxidized* and converted into ferric hydrate.

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* This woodcut first appeared in "Journ. Chem. Soc.," March, 1881. I am indebted for the use of it to the Editor of that Journal.

I have performed many careful experiments upon the action of ferrous hydrate on nitric oxide, the results of which have abundantly confirmed the above hypothesis. The following experiment will, I think, suffice for purposes of demonstration.

Pure nitric oxide is prepared from a mixture of sulphuric acid, potassium nitrate, and ferrous sulphate. The pure gas is collected in a large Crum's tube by displacement of water. A solution of ferrous sulphate is introduced into the cup at the top of the tube, solution of ammonia is added in excess, and the contents of the cup thoroughly mixed. The stopcock (which should have a large channel through it) is then opened, and the freshly precipitated ferrous hydrate allowed to fall through the gas, where it is collected upon a little saucer of wire gauze with a very fine mesh, supported in the gas by a stout copper wire. The apparatus is figured below.

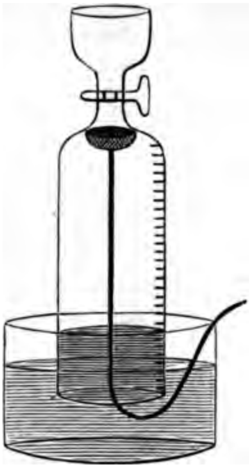

FIG. 3.

Immediately after the introduction of the ferrous hydrate into the copper gauze basin the former begins to undergo oxidation to ferric hydrate, whilst the gas is observed to diminish in volume. If the introduction of ferrous hydrate be continued until no further oxidation takes place, the volume of the residual gas will be found to be exactly *half* that of the original nitric oxide, and examination will show it to be *pure nitrogen.* The equation which represents the action of nitric oxide upon ferrous oxide may therefore be written as follows:—

$$2FeO + NO = Fe_2O_3 + N.$$

I imagine, therefore, that it is certain that the purity of the nitrogen obtained, as described in March, 1881, was due to the action of *ferrous hydrate* upon the gas evolved from ammonium nitrite, and not, as I then supposed, to the absorbent action of acidulated *ferrous sulphate*.

So much for the purity of the *nitrogen*.

As regards the *second* objection to my experiments of March, 1881—viz., that the *hydrogen* I employed might have contained oxides of nitrogen derived from the solution of *silver nitrate* through which it was passed,—I can only say that the possibility of such an occurrence was pointed out to me shortly after the publication of my paper referred to, and I have since employed mercuric chloride, solutions of chromic acid, and other reagents for this purpose, but without observing any difference in the quantities of ammonia obtained.

Moreover, I do not think it possible that any ammonia-forming gas could have been present in the hydrogen actually used in my experiments, since I find, by reference to my published paper, that the purified nitrogen and hydrogen were passed *together* through a solution of potash and pyrogalline, which solution I have found by direct experiment to have a powerful effect in decomposing nitric oxide. But the question of possible formation of ammonia by impurities in hydrogen has been abundantly settled by subsequent experiments, in which I have found that if pure nitrogen from ammonium nitrite be passed through a hot tube *before being mixed with hydrogen*, no ammonia is produced when the mixed gases are passed over hot spongy platinum, but the production of ammonia becomes very evident as soon as the tube transmitting the nitrogen is allowed to become cold. If nitric oxide be mixed with the nitrogen before its entrance into the heated tube, the heated mixed gases subsequently yield ammonia by contact with hydrogen in hot spongy platinum; for nitric oxide is not decomposed by even a full *red heat.*

This experiment affords, to my mind, the strongest evidence that the gas evolved from hot solutions of ammonium nitrite contains an allotropic or *active* form of nitrogen, which differs from ordinary nitrogen in possessing the property of forming ammonia by direct synthesis with hydrogen in presence of heated spongy platinum, and which is converted into ordinary inactive nitrogen by the action of heat, precisely as ozone is converted into ordinary oxygen by the same agent.

It is clear that if the nitrogen in the last quoted experiment had contained nitric oxide, ammonia would have been formed by combination of the heated gas with hydrogen in the spongy platinum; whilst if the production of ammonia had been due to the presence of an impurity in the *hydrogen*, its formation would have continued throughout the experiment, since the treatment of the hydrogen was never altered.

The ammonia-forming gas, then, was present in the gas evolved from the heated ammonium nitrite solution, and not in the hydrogen. Moreover, the ammonia-forming gas was deprived of its power of producing ammonia by direct union with hydrogen in presence of heated spongy platinum, by simple transmission through a glass tube heated to redness *before* being mixed with the hydrogen.

Now, my experiments quoted above, and indeed the recorded experience of all chemists, go to prove that *nitric oxide* is *not decomposed* by simple transmission through a red-hot tube; therefore it is extremely improbable that the ammonia-forming gas is nitric oxide.

The only known oxide of nitrogen which could escape the purifying reagents employed by me, and which is easily decomposed at a red heat, is *nitrous oxide*. Now, a laborious series of researches by Mr. T. Lewis Wright, undertaken with the object of ascertaining whether nitrous oxide and hydrogen in any circumstances yield ammonia under the influence of spongy platinum, have resulted in a negative conclusion (*vide* "Chemical Society's Journal," July, 1881). Accepting the accuracy of Mr. Wright's researches upon this point, I have confined myself to the examination of the question whether nitrous oxide gas is ever evolved from solutions of ammonium nitrite mixed with *ammonium nitrate*. I subjected solutions of *ammonium nitrite* containing little ammonium nitrate on the one hand, and solutions of ammonium nitrate containing little nitrite on the other, to the action of heat, but the resulting gas after treatment with ferrous sulphate over mercury was always found to be free from oxygen, either combined or uncombined. After treatment with a series of electric sparks, the volume of the gas remained unchanged on shaking with alkaline solution of pyrogalline.

Therefore the results of further experiments have led me to the conclusion that the ammonia formed by direct union with hydrogen of the gas produced by the action of heat upon solutions of ammonium nitrite (1st) is not due to any impurity in the hydrogen gas; (2nd) is due to an ingredient of the nitrogen, which is neither nitric oxide nor nitrous oxide, but is either an unknown compound of nitrogen that is decomposed by transmission through a glass tube heated to redness, or (more probably) an *allotropic active modification of nitrogen itself*, analogous to active oxygen or ozone.

CHAPTER III.

FURTHER EXPERIMENTS ON THE NATURE OF THE GAS PRODUCED BY ACTION OF HEAT UPON SOLUTION OF AMMONIUM NITRITE, CONDUCTED IN 1883.

A Secondary Reaction occurs on heating Solutions of Ammonium Nitrite of Large Volume, leading to the formation of Ammonia, Nitric Oxide, and Ammonium Nitrate: this Secondary Reaction does not take place on heating Small Volumes of Solution of Ammonium Nitrite—Method of Experimentation in 1883—Gas obtained from Small Volumes of Ammonium Nitrite Solution entirely free from Oxides of Nitrogen—Typical Experiment with a Mixed Solution of Commercial Potassium Nitrite and Ammonium Chloride, of Small Bulk—Experiments with Solutions of Pure Ammonium Nitrite—Method of preparing Pure Ammonium Nitrite Solution—Different Effects observed with Solutions of different reaction to Test-papers—Examination of the Gas evolved from Pure Solutions of Ammonium Nitrite at various Temperatures—Effects of the Gas upon Solution of Potassium Iodide—Action of the Gas upon Hydrogen in presence of Heated Spongy Platinum—Quantitative Experiments with Active Nitrogen from Pure Solutions of Ammonium Nitrite.

IN my experiments performed at the close of the year 1880, and published in 1881, I employed a solution of ammonium nitrite of large bulk (one and a half to two litres), made by saturating distilled water at the ordinary temperature with commercial potassium nitrite and an excess of ammonium chloride.

Judging from the formation of ammonia and nitric oxide in the reaction resulting from the action of heat upon such a solution, it appears that in the case of concentrated solutions of ammonium nitrite of large volume, a secondary reaction occurs on the application of heat; so that, besides the primary production of water and nitrogen gas—

$$(1.)\ NH_4NO_2 = 2H_2O + N_2,$$

there is also a formation of ammonium nitrate, ammonia, nitric oxide, and water, thus:—

$$(2.)\ 3NH_4NO_2 = NH_4NO_3 + 2NH_3 + 2NO + H_2O.$$

Further experiments, conducted in the year 1883, have led me to the conclusion that in the case of solutions of smaller volume this secondary reaction does not take place.

The differences observed in operating upon the large and small scale respectively are so well known that I shall offer no apology for this explanation of the different results obtained, but I will simply detail my method of procedure for the benefit of future workers, and describe the phenomena observed.

In 1883 I employed small flasks, not exceeding 350 cubic centimetres in capacity. Most commonly the solutions measured 200 cubic centimetres or less; that is, about one tenth of the volume employed in 1881.

In all the experiments there was a uniformity of results as regards the production of oxides of nitrogen. The flasks were filled with the solution under examination, corks with delivery-tubes adjusted, the flasks immersed in water, the water around the flasks gradually heated, and the gas issuing at various temperatures collected by displacement of mercury in graduated tubes, carefully measured, exposed to the action of various absorbents, and again measured. In every case the complete absence of nitric oxide or any known oxide of nitrogen was distinctly proved, provided only that the solution operated on was originally *alkaline in reaction*. Even if the solutions (of the volume indicated) were heated rapidly, ferrous sulphate produced *no change of volume* in the resulting gas; and although in some other respects the gas evolved at low temperatures differed remarkably from that which escaped at higher ones, there was no difference as regards freedom from *oxides of nitrogen*. My conclusion, therefore, is that the secondary reaction which results in the formation of nitric oxide occurs only on heating solutions of ammonium nitrite of large volume and great concentration.

In my first experiments, in 1883, I used solutions made by dissolving known weights of commercial potassium nitrite and ammonium chloride in known volumes of water. The following are the details of a typical experiment:—

Seventeen grammes of commercial potassium nitrite and eleven grammes of ammonium chloride were dissolved in 310 cubic centimetres of distilled water. The flask containing the solution was immersed in a water bath provided with a thermometer, and the temperature raised. Gas began to escape freely at 80° C. Two litres of gas were collected at temperatures below 100° C., and an equal volume escaped on boiling the contents of the flask over a flame after the evolution had ceased in the water bath.

About 12 per cent. by volume of the first portions of gas collected was absorbed by agitation with water, and rapidly by solution of potash and lime-water, producing a precipitate in the latter case. The source of this carbon dioxide gas was traced to the presence of potassium carbonate in the commercial potassium nitrite.

Collected over mercury and treated with solution of ferrous sulphate, no trace of nitric oxide could be detected, even in the last portions of gas evolved, which seemed to be pure nitrogen. The reaction of the residual solution after boiling, like that of the original mixture, was distinctly alkaline.

In order to avoid the presence of *carbon dioxide* in the nitrogen gas, I determined to work with solutions of *pure ammonium nitrite*, which I prepared as follows:—Small lumps of vitreous arsenious acid are covered with cold strong nitric acid (sp. gr. 1·46) in a glass flask provided with a cork (not caoutchouc) and a glass delivery-tube bent twice at right angles, the extremity of which just dips below the surface of a strong solution of ammonia gas in water (sp. gr. 0·880) contained in a second glass flask, which remains uncorked, and should be kept immersed in cold water. If the action becomes very violent in the generating flask, that also may be cooled by a stream of water.

Gas escapes freely from the ammoniacal solution, owing to the occurrence of the reaction—

$$HNO_2 + NH_3 = 2H_2O + N_2,$$

but a large quantity of ammonium nitrite remains in the second flask, undecomposed. The flask is, of course, filled with dense white fumes of ammonium nitrite. Near the end of the action these white fumes begin to acquire a *reddish tinge*, and at this stage the passage of N_2O_3 into the ammoniacal solution must be at once arrested, otherwise the liquid becomes hot and undergoes spontaneous decomposition in a few seconds, large volumes of nitric oxide being produced.

If the process be arrested before this spontaneous decomposition has commenced, the product in the receiving flask is a yellowish alkaline liquid, smelling very slightly of ammonia, and evolving much nitrogen when heated. If some of this alkaline solution of ammonium nitrite be passed up into a graduated glass tube by displacement of mercury, and a few drops of any dilute mineral acid be introduced by the same means, a sudden and violent disengagement of gas ensues, about 40 per cent. of which is absorbable by solution of ferrous sulphate.

This reaction is easily accounted for by the well-known equation—

$$3HNO_2 = H_2O + HNO_3 + 2NO;$$

and this explains the violent decomposition which ensues if the nitrous anhydride be passed into the aqueous ammonia until the solution acquires an *acid reaction*.

It is necessary, therefore, to avoid the development of an *acid reaction* in the ammonium nitrite solution. On the other hand, if the solution of ammonium nitrite be too strongly ammoniacal it is decomposed by heat with great difficulty, and no gas escapes at temperatures below 100° C. except ammonia itself.

If the solution be as nearly neutralized as possible by N_2O_3, much nitrogen gas is evolved at temperatures between 80° and 85° C.

If to a slightly ammoniacal solution of ammonium nitrite, prepared as above described, crystals of cupric chloride be added, a steady effervescence of perfectly *pure nitrogen* occurs at the ordinary temperature (20° C.). The cupric chloride probably effects this change by combining with the slight excess of ammonia in the solution, without liberating any *nitrous acid*, as would be the case with a mineral acid; the neutral ammonium nitrite solution thus obtained decomposing spontaneously—

$$x\mathrm{NH_4NO_2} + 2\mathrm{CuCl_2} + 2\mathrm{NH_3} + \mathrm{H_2O} = \mathrm{CuO\ CuCl_2} + 2\mathrm{NH_4Cl} + x\mathrm{N_2} + 2x\mathrm{H_2O}.$$

And this hypothesis is supported by the fact that a precipitate of cupric oxychloride is gradually formed, whilst the gas evolved is not altered in volume by solution of ferrous sulphate.

Examination of the Gas evolved from Pure Solutions of Ammonium Nitrite at Different Temperatures.

Having obtained a large volume of pure solution of ammonium nitrite as nearly neutral as possible by the process above described, I examined it by the method already indicated.

About 100 cubic centimetres of the solution were introduced into a small flask with a cork and delivery-tube, which was completely filled thereby. The flask was immersed in water with a thermometer near it; the temperature of the water was raised, and the gas evolved, *without subjection to the influence of any purifying agent whatever*, was collected in graduated glass tubes by displacement of mercury, and subjected to the action of various absorbents. When the absorbents were aqueous solutions the volume was simply noted before and after agitation with the absorbent; in the case of desiccating agents the gas was dried before introducing the absorbent, the volume of the dry gas read off, and the absorbent then added. As I have already stated, the results of these experiments were entirely negative as regards the presence in the gas of oxides of nitrogen.

There was a remarkable difference in properties between the gas evolved from pure solutions of ammonium nitrite at temperatures below 90° C. and that which escaped at higher temperatures.

If a solution of starch and potassium iodide be introduced into the gas collected over mercury as above described, no change of colour is observed in the solution, no matter at what temperature the nitrogen has been evolved; and even if *oxygen* be admitted into the gas standing over solution of potassium iodide and starch, no change of colour takes place. This experiment negatives the presence of nitric oxide in the gas.

But if into the gas evolved below 90° C., and standing over mercury, some solution of starch and potassium iodide, previously acidulated and quite colourless (thus proving the absence of any ingredient in the *iodide* which might yield free iodine on acidulation), be introduced, there is an immediate production of a blue colour in the liquid. There is, I believe, no known gas, except oxygen, which liberates iodine from potassium iodide only in acid solutions.

My explanation of this liberation of iodine from the potassium iodide in presence of free acid, and not in a neutral solution, is as follows:—

The nitrogen evolved from solutions of ammonium nitrite at temperatures below 90° C. is partially *active.* This active nitrogen forms, with water, *ammonium nitrite*—

$$N_2 + 2H_2O = NH_4NO_2.$$

Solution of ammonium nitrite does not liberate iodine from potassium iodide in a neutral solution; but after *acidulation* the nitrous acid set free from it liberates iodine as described.

It may be urged that some *ammonium nitrite* might have accompanied the gas in the above experiments and given rise to the phenomena observed, but I repeated the experiments with the precaution of passing the gas through U-tubes containing calcium chloride and fragments of pumice saturated with H_2SO_4, and with precisely similar results.

No change of volume could be detected in the gas after the liberation of the iodine from the acidulated potassium iodide.

If the gas evolved from solution of pure ammonium nitrite at temperatures below 90° C. was transmitted through a glass tube heated to redness before being collected over mercury, it liberated no iodine from acidulated solution of potassium iodide and starch.

Again, the gas evolved from solution of ammonium nitrite at temperatures above 90° C. *forms no ammonia* when mixed with hydrogen and transmitted through a tube containing heated spongy platinum; neither does it effect liberation of iodine from solution of potassium iodide even after acidulation. It is, in fact, ordinary inactive nitrogen in a state of purity. But the gas which escapes from the pure solution of ammonium nitrite at temperatures *below* 90° C. forms appreciable quantities of ammonia on being mixed with hydrogen and transmitted through a tube containing heated spongy platinum. The power of producing ammonia, like that of liberating iodine from acidulated solution of potassium iodide, is destroyed by subjecting the gas to a high temperature, precisely as ozone is converted into oxygen by that treatment.

In short, the gas evolved from pure solution of ammonium nitrite at temperatures below 90° C. is partially *active;* that evolved above 90° C. is entirely *inactive;* and the active nitrogen is rendered inactive by a high temperature.

QUANTITATIVE EXPERIMENTS.

I made some quantitative determinations of the actual weight of ammonia formed by direct union of a given volume of nitrogen gas with hydrogen in presence of heated spongy platinum. The experiments were conducted as follows:—

Two flasks of equal capacity were charged with equal volumes of the same ammonium nitrite solution, and immersed in the same vessel of water with a thermometer between them. One of these flasks bore a cork with delivery-tube opening under the mouth of an inverted graduated vessel filled with water and inverted over water. The other flask was fitted with a cork bored with two holes, one admitting a tube delivering pure hydrogen, the other a delivery-tube which conducted the mixed gases through (1) a U-tube containing calcium chloride, (2) a U-tube packed with fragments of pumice-stone saturated with strong sulphuric acid, (3) a piece of hard glass combustion tubing containing spongy platinum, (4) a counterpoised U-tube containing soda-lime, and (5) a nitrogen bulb containing a known volume of dilute hydrochloric acid, the ammonia in which had been previously estimated as ammonio-platinic chloride.

Now, if any oxygen—free or combined—had been present in the gas, *water* must have been formed in the heated spongy platinum, and have increased the weight of the soda-lime tube. But this tube *did not increase in weight* in any of the experiments.

The following results were obtained:—

Two hundred cubic centimetres of nitrogen (=0·25 gramme) gave 0·04 gramme of $PtCl_4 2NH_4Cl$, equivalent to 0·003 gramme of ammonia; *i.e.*, 0·0025 gramme of nitrogen was active, or 1 *per cent.* of the total volume.

The above gas was obtained from a solution of pure ammonium nitrite as nearly neutral as possible, heated below 90° C. As already stated, the gas evolved at temperatures above 90° C. never yields any ammonia.

One hundred and seventy cubic centimetres of nitrogen (= 0·212 gramme) gave 0·072 gramme of $PtCl_4 2NH_4Cl$, equivalent to 0·00547 gramme of NH_3. Therefore, 0·0045 gramme of nitrogen was active, or 2·1 *per cent.*

The above gas was obtained *without heat* by the action of cupric chloride upon solution of ammonium nitrite as above described.

CHAPTER IV.

EXPERIMENTS WITH ATMOSPHERIC NITROGEN.

Direct Synthesis of Ammonia from Atmospheric Nitrogen, obtained without the agency of Heat—Details of Experiment—Criticisms on this Experiment—Experiments with Electricity of High Tension —Explanation of Donkin's Synthesis—Complete Synthesis of Ammonia by the Spark—Explanation of Ste. Claire Deville's Observations.

LIKE all investigators who have made the experiment, I have failed to produce any ammonia by passing atmospheric nitrogen, which had been recently heated and then mixed with hydrogen, through red-hot tubes, even in presence of spongy platinum.

I believe, however, that I was the first to assert the possibility of obtaining ammonia in small quantity from atmospheric nitrogen which has *not been heated*, by direct union with pure hydrogen in presence of spongy platinum. The experimental proof of this statement is contained in a paper which I read before the Royal Society in October, 1881, and which has not been published. The details of the experiment are as follows:—

"Atmospheric air was made to pass into a glass gasholder by traversing a vessel packed with sawdust impregnated with freshly precipitated ferrous sulphide. The nitrogen thus obtained, still containing some oxygen and some sulphuretted hydrogen, was then allowed to stand for some days over water holding ferrous ferrocyanide in suspension. It was then further purified by being passed through (1) strong solution of caustic potash, (2) alkaline pyrogalline, (3) strong sulphuric acid, and (4) Nessler reagent. Thus freed from H_2S, CO_2, O, and NH_3, the nitrogen entered a T-piece, in which it was mixed with hydrogen, evolved by action of sulphuric acid upon zinc, and purified by bubbling through (1) solution of chromic and sulphuric acids, and (2) Nessler reagent.

"The pure atmospheric nitrogen and hydrogen thus formed were conducted into a tube containing spongy platinum, and thence into a vessel containing Nessler reagent. Ammonia was invariably formed, unless the nitrogen had been previously heated, *when none was ever observed.* The quantity of ammonia formed was small, never exceeding a milligramme and a half from ten litres of nitrogen."

This experiment, the description of which is quoted from my paper of October, 1881, has been repeated with *the same result,* but the formation of ammonia is attributed to the ferrous ferrocyanide, which is supposed to give off a nitrogenous gas when kept suspended in water, this gas yielding ammonia by union with hydrogen in presence of spongy platinum. The only reason given for this hypothesis is that *more ammonia was formed the longer the gas stood over the water in which the ferrous ferrocyanide was suspended.* My answer to this criticism is that I have obtained the same results when the nitrogen was kept over water holding *ferrous hydrate* in suspension.

I have made numerous experiments on the action of electricity of high tension upon nitrogen and upon nitrogen mixed with hydrogen, the general results of which I will now recapitulate.

Firstly, I soon found that recently-heated nitrogen gives no ammonia when mixed with hydrogen and *passed through* an induction-tube as in Mr. Donkin's experiment. If *confined* in an induction-tube for some hours and exposed to the silent discharge, ammonia was formed, but not by a transient exposure to the electric current.

After standing for some hours over water, however—a precaution which Mr. Donkin expressly mentions, though with a different object—the mixed gases invariably yield ammonia in the induction-tube.

Secondly, when atmospheric nitrogen mixed with hydrogen has stood over water (holding ferrous hydrate in suspension) for many hours, and is then passed through (1) a tube containing cold spongy platinum, (2) bulbs containing strong sulphuric acid, (3) an induction-tube, and (4) bulbs containing Nessler reagent, *no ammonia* is formed in the induction-tube; but if the tube containing the spongy platinum be removed, ammonia *is formed* in the induction-tube.

My explanation of Mr. Donkin's synthesis of ammonia is that *the ammonia was formed by active nitrogen produced in small quantity during the storage of the gas over water with hydrogen*—a precaution essential to the success of the experiment. The formation of the ammonia was prevented by the insertion of the spongy platinum between the gas-holder and the induction-tube, because the spongy platinum effected the combination of the active nitrogen present in the gas with hydrogen, even at the ordinary temperature, so that the mixture which entered the induction-tube then consisted only of hydrogen and inactive nitrogen, which gases cannot be made to combine by a *transitory* application of the silent discharge of electricity.

I believe, therefore, that, under certain conditions, small quantities of active nitrogen are formed in the gas of our atmosphere, though I have not yet succeeded in obtaining large quantities thereof.

I am in hopes that the statement which is still common in the books, that "the synthesis of ammonia by the direct union of its elements has never yet been effected," will soon be discontinued, for I have succeeded in effecting the *complete* synthesis of a mixture of nitrogen and hydrogen by a simple experiment which I will now describe.

Into an ordinary eudiometer tube, full of mercury, pure nitrogen gas—obtained by any method, either from the atmosphere by red-hot copper, or from ammonium nitrite—is introduced and measured. Next admit three times its volume of pure hydrogen gas, and introduce into the gaseous mixture a fragment of wood-charcoal previously ignited in hydrogen gas, or better, in a mixture of three volumes of hydrogen with one volume of nitrogen gas. Now pass the spark continuously through the wires of the eudiometer. About four to six cubic centimetres of the mixture are combined and absorbed by the charcoal per hour, until finally the whole of the gas may be made to disappear; after which, if the charcoal be removed, it will be found impregnated with ammonia.

This experiment not only puts the possibility of the synthesis of ammonia from the direct union of its elements beyond question, but it also explains Deville's observation that the dissociation of ammonia by a series of electric sparks is never perfect. After a certain time the dissociation and re-combination proceed *pari passu*, and the gaseous mixture of nitrogen, hydrogen, and ammonia remains of uniform composition. In presence of any *absorbent for ammonia*, continuous combination is effected, till all the nitrogen and hydrogen have been converted into NH_3.

I contend, therefore, that the results of the researches recorded above form a complete confirmation of the accuracy of the various observations detailed in my papers read before the Chemical and Royal Societies, including those not published in their Transactions.

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